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OF A1/C FIBER COMPOSITES

by

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INVESTIGATION OF MICROSTRUCTURAL BRAZING OF Al/C FIBER COMPOSITES

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ABSTRACT:

Abstract The metal materials (Mg, Al, Ti and alloys) and the reinforcing components (Carbon fiber, SiC whiskers, particles, etc.) used in forming metal matrix composites have great mismatch between their physical, chemical and mechanical properties. The study of fabricating Al/C fiber composites and using them as structural materials is becoming an important new field in material science. An investigation on the microstracture bonding technology is not only of great significance for the improvement of mechanical property and fabricating process of the composites but also of great importance to the bonding of composite to composite or to other materials in the foreseeable practical applications.

Key words composite; reinforcing component; microstructure brazing; wettability

INTRODUCTION

Composite materials are one of the important branches of new-materials science. These materials have various excellent performance features that cannot be matched by single-constituent material. Therefore, there have been very rapid developments in composite materials that are glass fiber/resin-based, carbon-based, and ceramic-based. In the early sixties, metal-based composite materials began to be studied in the United States. In

the late seventies, enormous success was realized in practical applications in fields such as aerospace. For progress in high science and technology, research in metal-based composite materials has also been greatly stressed in the Soviet Union, Japan, and western European countries. At present, most researchers concentrate their efforts in three aspects; enhancement of constituents, composite processing, and interface properties. The enhancement constituents in metal-based composite materials are mostly nonmetallic materials such as C, B, Si, and Al_2O_3, or their combinations. From their appearance, most of these materials are long-fibered and consist of short crystal whiskers, particles, and small slices with dimensions in the micrometer range. By citing, as an example, an Al/C fiber composite material, as stated in specialists' research, for each $100cm^3$ of composite material there are approximately $3x10^9cm^2$ of boundary surface area [1]. At the boundary surfaces, the binding quality of C fibers and the aluminum matrix will directly affect the overall macroscopic properties of the composite material. There is the problem of joining the boundary surfaces of heterogeneous materials while composite materials are formed. Since the geometric dimensions of the enchancement constituents are very small, this can be considered as a problem in welding microstructures. There are frequently great differences in the physicochemical properties of metal-based (such as Al) and enhancement constituents (such as C fibers), thus causing great difficulties in binding them together. This becomes a difficult

technique in studying and making composite materials that has attracted reearcher attention.

As to the universality of the problem, the authors conducted experiments and studies on connecting boundary surfaces of Al-based/C fiber composite material. Penetrating systematic studies were conducted on this aspect. This not only has direct significance to the quality of applications and technique of compositing the composite material, but also has practical significance on binding between structural constituents for practical applications of composite materials.

I. Experimental Materials and Experimental Porcess

I.1. Experimental materials. As used in the experiment, the aluminum rods (OD 20mm) and aluminum slices (δ=1 to 1.5mm) are Chinese-made pure aluminum (L_2); the carbon fibers are products of the Shanghai Carbon Plant, with measured strength between 2600 and 2700N/mm^2, linear density 141.7mg/m, and fiber diameters between 6 and 7micrometers, at 3000 fibers per bundle. Table 1 lists the materials used in experimental studies of welding.

I.2. Experimental process

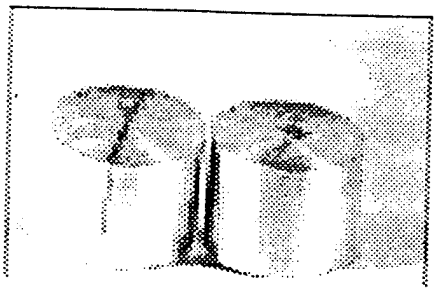
In making Al-based composite materials, brazing of Al and Al, and brazing of Al and C fibers are employed. In an OD 20mm x 15mm cylinder, a linear cutting machine was used to cut a tiny notch 0.1 to 0.4mm in size. With brazing, the openings at three sides were closed so that the cracks were within the cylinder.

Table 1

	Experimental materials	Melting temperature (℃)
Brazing filler metals	Al – Si – Mg	560
	Al – Zn – Si – Cu	518 ~ 523
	Zn – Sn – Cu	198 ~ 370
	Zn – Sb – Cu	250
	Zn – Cd	265 ~ 335
Flux	$KCl - ZnCl_2 - NaF$	380 ~ 420
	$ZnCl_2$	-

The appearance is shown in Fig. 1. By using the CT process and X-ray flaw detection, the existence and spatial location of the cracks were detected. Next, a tiny hole was drilled from the exterior surface toward the crack, and brazing filler metal and solder were placed in the tiny hole. Then followed heating until the filler metal was melted so that the cracks were welded over. The specimen was cut along the horizontal direction for metallurgical observation. From Fig. 2 we can see that all cracks were welded over, forming a metallurgical connection.

For brazing between C fiber and aluminum matrix, first the wetting properties on the carbon surfaces due to the brazing filler metals (Al, Al-Si-Mg, Al-Zn-Si-Cu, Zn-Sn-Cu, Sn-Sb-Cu) were measured. Table 2 lists the experimental results. As indicated by the experiments, in vacuum conditions they do not wet graphite surfaces after the melting of pure Al and Al-Si-Mg alloy. The melting metals are spheroidal in shape. In the case when solder was added under an atmosphere, they do not wet a



(a) Cutting sample (b) Sample contained "flaw"

Fig.1 Experimental sample

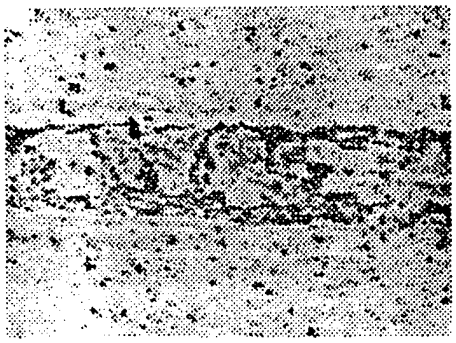


Fig.2 Micrograph of brazed inner flaw ×100

graphite surface after melting of the Al-Zn-Si-Cu, Zn-Sn-Cu, Sn-Sb-Cu alloy, as shown in Fig. 3a. However, the situation is entirely different if activating treatment is applied to the graphite surface. Whether under vacuum conditions, or in an atmosphere with the addition of solder, they have excellent wetting properties for several experimental materials on the treated graphite material, as shown in Fig. 3b.

According to the wettability experimental results measured above, by applying the similar activation treatment was applied to C fiber surfaces in order to enhance the wettability. A tiny notch was cut into a pure aluminum plate (1.5mm x15mm x30mm), as shown in Fig. 4, the activated treated fibers were placed in the tiny notch, and a piece of a machined aluminum plate was placed over it. Then appropriate quantities of solder and brazing metal filler were placed beside it to be heated. After the filler metals were melted, the molten metals were then allowed to flow into the gap between the two plates and into the tiny notch, thus

Table 2 Wetting experimental results

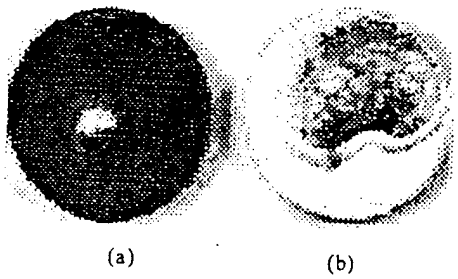
Matrix	Brazing filler metals	Wettability	
		Surface treatment	No surface treatment
Graphite	Al*	Good	No
	Al-Si-Mg*	Good	No
	Al-Zn-Si-Cu**	Good	No
	Zn-Sn-Cu**	Good	No
	Sn-Sb-Cu**	Good	No
Titanium		Good	Poor

* In vacuum condition, ** In atmosphere condition

wetting the C fibers in the notch for metallurgical binding. A metallurgical observation was made by horizontal cutting of the specimen. All the C fibers in the tiny notch were found to have been wetted by the filler metal and welded into a whole piece. In Fig. 5 we can observe the homogeneous distribution of C fibers. With a high magnification (Fig. 6), the microscopic local nonwettability phenomena were not observed in the circumferential surface of the C fibers. Good metallurgical binding was found along the boundary surfaces.

If the surfaces of the C fibers were not subjected to the activation treatment, the molten filler metals did not wet the fiber surface. Instead, the molten filler metal bundled up the C fibers, and these two materials are incompatible after they are solidified. In the metallurgical observation, one or several black holes (where the C fibers accumulated) were found in the solidified filler metals. There are uneven C fiber broken

surfaces appearing in the black holes. In Fig. 7 we can see clearly that the binding of filler metal was not achieved between the untreated C fibers and the aluminum.



(a)No wetting on graphite surface
(b)Good wetting on treated graphite surface

Fig.3 Wetting experiment

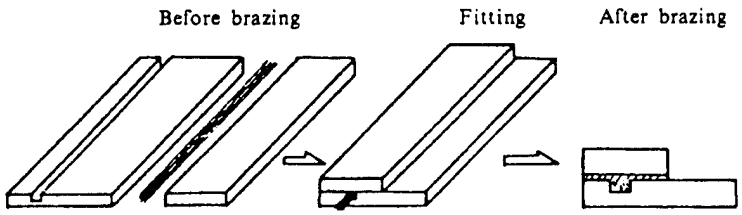


Fig.4 Schmetics of brazing processes of Al metrix and carbon fiber

From Figs. 6 and 7, we can see that there are the same materials and techniques used for the experiments. In the former case, there is only the surface activation treatment for carbon fibers. In the latter case, there is no treatment. These two exhibit different results. This indicates that it is very important to apply apropriate treatment to C fiber surfaces. Different treatments produce different results.

II. Analysis and Discussion

In the fabrication of Al-based/C fiber composite materials, a frequently adopted process is to first make "precursor" filaments before compositing the precursor filaments into materials of plate, rod, or pipe shape. In the fabrication

process, there are binding problems between C fibers and the Al matrix, as well as between Al matrix and Al matrix. First, consideration should be given to the properties of Al material as

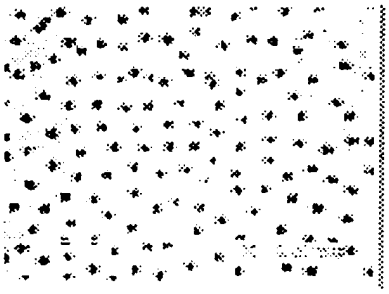


Fig.5 Microphotograph of carbon fiber (after brazing) ×100

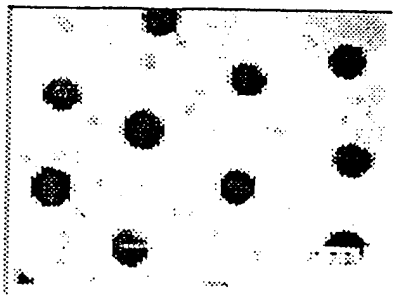


Fig.6 SEM photograph of carbon fiber (after brazing) ×1000

there is great affinity between aluminum and oxygen, so it is easy to form an aluminum oxide thin film on the surface, with its melting point as high as 2050°C, which is much higher than aluminum's melting point, which is 660°C. In addition, alumina is compact and stable and difficult to remove. In conventional situations, the thickness of aluminum film is between 200 and 800 angstroms. The presence of thin films of alumina seriously hampers the wetting on Al after the melting of filler metal, thus making it difficult to form the continuous metallurgical binding. Therefore, when selecting the filler metals and solder materials and the technical process, consideration should be given to purification of the thin alumina films, and to protecting the surface activity of the new formed alumina. For thin films of

Cd) as the film removing agent, and metal chlorides (Zn, Cd, Sn) are added as activating agents to remove the oxide film surface

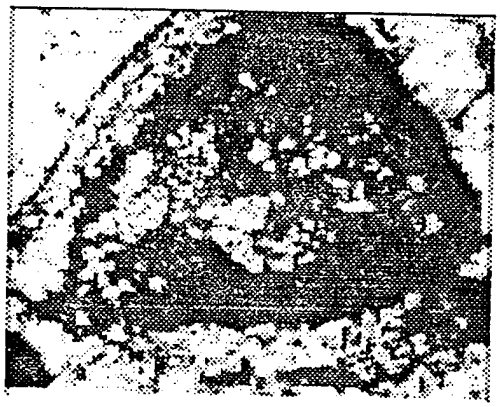


Fig.7 Photograph of uncompatibility of carbon fiber with no surface treatment and Al matrix ×50

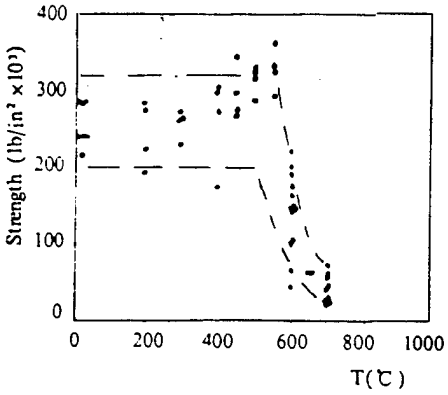


Fig.8 Relationship between strength of Al coated carbon fiber and temperature

because they have very high wettability, However, the time should be very short, otherwise an oxide film will be reform. Considering that the melting points are lower (less than 660°C) for alumina and aluminum alloys, the temperature should not be too high when the precursor filaments are composited into the materials being formed. As mentioned in the literature [2], by using the vacuum evaporation and coating method to coat the aluminum onto the graphite fiber surfaces, then a heat treatment for 24h at different temperatures under vacuum conditions is done to determine the variation of intensity. It was found that the strength apparently drops at 600°C. With rising temperature, the

strength drops off seriously, with the details shown in Fig. 8. As indicated by X-ray diffraction analysis, after 24h of heat treatment at 600°C, there appeared small amounts of aluminum carbide (Al_4C_3) on the boundary surfaces. However, for treatment at 700°C, large amounts of Al_4C_3 reactants appeared on the

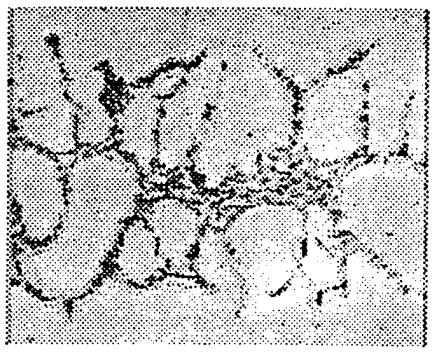


Fig.9 Microstructure of Al－Al brazing joint ×400

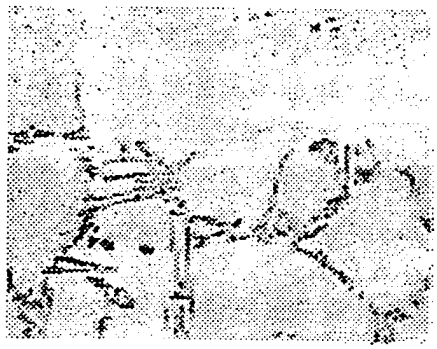


Fig.10 Microstructure of interface ×600

boundary surfaces; these are brittle chemicals, thus seriously reducing the strength of the C fibers. In order to prevent the formation of brittle chemicals of Al_4C_3, the heating temperature during brazing should be properly selected (approximately between 300 and 500°C) and the heating temperature should be even and not held too long. Besides this, proper treatment on the C fiber surfaces is very important.

Further metallurgical observations and analysis were conducted on the brazed joint of Al-Al brazed joints. In the brazed joint zone, a solid solution is the matrix phase. At the crystallite boundaries, low-melting eutectics were precipitated, as shown in Fig. 9. The amount precipitated in the eutectic phase is related to the components of the filler metal, and also

to the technical factors of the width of the brazed joint, and to heating and cooling rates. At highly magnified metallurgical observation, there were complete and compact alloy textures in the brazed joint zone. Analyses were also made of the boundary surface zone of the brazed joint. Melting and diffusion occur at

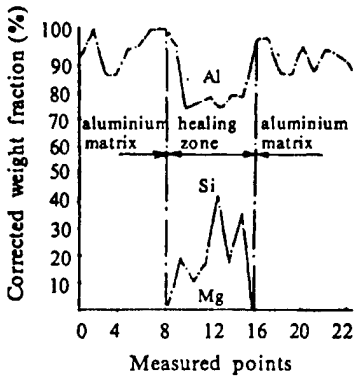


Fig.11 Elements distribution in brazing joint

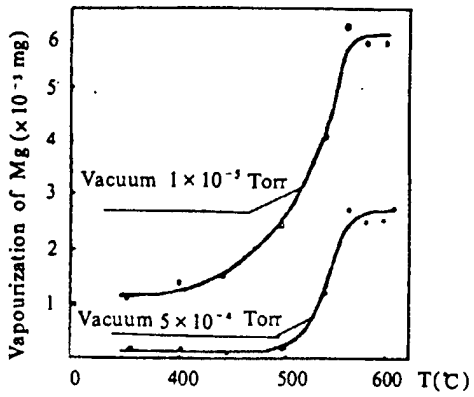


Fig.12 Relationship between vapourization of Mg and temp., vacuum in Al−Si−Mg brazing filler metal

the boundary surface of the solid-liquid phase. The liquid-phase brazing metals diffuse deeply into the matrix along the solid phase crystallite boundaries with dissolving occurring, so that they formed zigzag see-saw shapes on the surface of the solid phase, actually forming a boundary surface band.

Fig. 11 shows the results of analyzing the element distribution in the brazed joint zone detected with an electron probe. The brazed joint is formed by Al-Si-Mg filler metals. As

indicated by the analytical results, the Mg content tends to zero in the brazed junction. This is because Mg evaporates and is expended from burning during brazing heating. In order to investigate the evaporation behavior of Mg, a relationship between evaporation and vacuum, as well as between evaporation

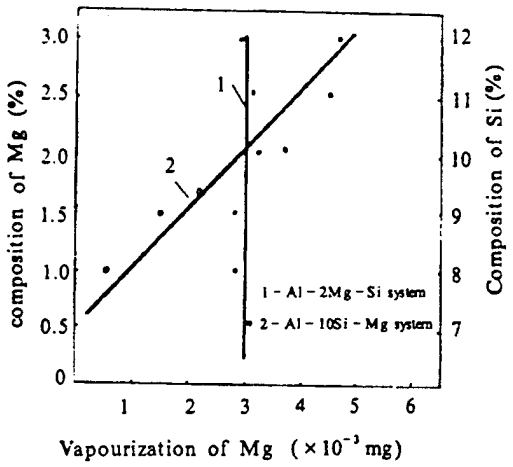


Fig.13 Influence of different content of Si, Mg in Al−Si−Mg alloys on vapourization of Mg

and temperature of Mg, was derived [12]. From Fig. 12, it is seen that Mg evaporates in different ways in the Al-Si-Mg filler metals under different vacuum conditions. At the same temperature, the higher the vacuum the more Mg that evaporates. Under the same vacuum conditions, temperature is also an important factor with regard to Mg evaporating. In particular, when the temperature rises in the range between 500 and 580°C, the variation in the amount of Mg that evaporates is rapid, rising linearly. This indicates that the amount of Mg that evaporates is high in the filler metals before and after

melting of Al-Si-Mg filler metals. In addition, experiments were also conducted on the effect on evaporation by Mg content in the Al-Si-Mg filler metals. From Fig. 13, there is no effect on the amount of Mg that evaporates when the Si content is varied in the Al-2Mg-Si series. By varying the Mg content in the Al-10Si-Mg series, there is a close relationship with the amount of Mg that evaporates. With an increase in the Mg content, the amount of Mg that evaporates increases proportionally. The melting point of Mg is 649°C, and under standard atmospheric pressure, its evaporation point is 621°C. Under vacuum conditions of 1.33×10^{-3}Pa, the evaporation point of Mg is 250°C. In the Al-Si-Mg filler metals, mostly there exists a state of Mg_2Si chemical product, besides a small amount of solid Mg dissolved in Al. Hence, from Fig. 12 there is low evaporation before 500°C; the evaporation does not vary much with temperature. However, in the range between 500 and 580°C, evaporation is the most intensive. After analyzing the vacuum medium, it also proves that there is the existence of Mg vapor.

The purpose of adding Mg to the Al-Si series filler metals is also to vaporize Mg at high temperatures. The Mg vapor reacts with the alumina thin film on the surface of the aluminum: Component analysis of x-ray diffraction was conducted on the residual oxide layer that was subjected to surface changes. As indicated in the results, $MgAl_2O_4$ exists in the surface layer. Under the specific conditions of vacuum brazing, the above-mentioned reaction actually exists. This reaction is also the

$$Mg + \frac{1}{2} O_2 \longrightarrow MgO$$

$$Mg + H_2O \longrightarrow MgO + H_2$$

——发生于真空介质中 1

$$3Mg + 4Al_2O_3 \longrightarrow 3MgAl_2O_4 + 2Al$$

——发生于基体表面上 2

KEY: 1 - occurring in a vacuum medium 2 - occurring on a matrix surface

necessary condition that the molten Al-Si-Mg filler metals can fully wet the surface of aluminum and the aluminum alloy.

There is a technical problem with high difficulty for metallurgical binding between the C fibers and the Al matrix. As indicated in the experimental studies, the condition for binding of the two is to treat the carbon fiber surfaces.

Generally speaking, this is related to the binding of the boundary surface between the matrix in the metal-based composite material and its strengthening components. At present, there are still very few reports in the literature in China and abroad on this aspect. However, this is a very important topic. This relates not only to the macroscopic properties of composite materials, but also is closely associated with binding between the composite material and the other heterogeneous materials. This problem will definitely be confronted in practical engineering applications.

III. Conclusions

(1) Binding between metal-based composite material and microstructural heterogeneous materials is an important topic, which should be emphasized in the realm of composite materials and welding technology.

(2) Brazing theory and techniques of Al-Al are applied to binding among precursor filaments in Al-based composite materials so that practical forms of material can be realized. This report merits more penetrating research.

(3) C fibers must undergo the necessary pretreatment prior to the compositing of Al/C fiber composite materials.

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